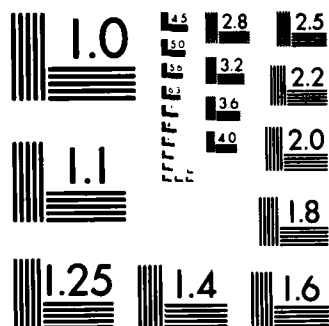END

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MECHANISMS AND KINETICS OF DIPHTHALOCYANINE ELECTRODE PROCESSES

ADA131726

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July 1983
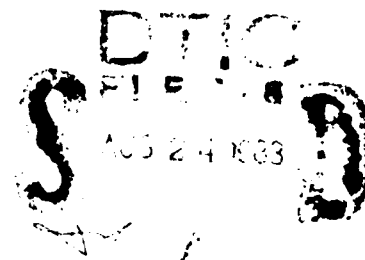
Final Report for Period 1 May 1980 to 31 March 1983

Contract F49620-80-C-0060

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Prepared for

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Bolling Air Force Base, D. C. 20332

83 08 19 11 9

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 83-0721	2. GOVT ACCESSION NO. AD-A131726	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Mechanisms and Kinetics of Diphthalocyanine Electrode Processes		5. TYPE OF REPORT & PERIOD COVERED Final Progress 1 May 1980 to 31 March 1983
		6. PERFORMING ORG. REPORT NUMBER C83-522/201
7. AUTHOR(s) M. M. Nicholson T. P. Weismuller F. A. Pizzarello		8. CONTRACT OR GRANT NUMBER(s) F49620-80-C-0060
9. PERFORMING ORGANIZATION NAME AND ADDRESS Autonetics Strategic Systems Division Rockwell International Corporation Anaheim, California 92803		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303/B
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research/NC Building 410 Bolling AFB, DC 20332		12. REPORT DATE July 1983
		13. NUMBER OF PAGES 31
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release: Distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

Journal of the Electrochemical Society, V 128, pp 1288-1290, 1981
Proceedings of IEEE 1983 National Aerospace and Electronics Conference,
V 1, pp 368-374, 1983

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Phthalocyanines
Rare earths
Oxidation-reduction
Electrochemistry
Spectra

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Redox processes of lutetium diphthalocyanine were investigated by chemical, electrochemical, and optical spectroscopic methods. Oxidized films of the dye slowly reverted from the red to the green state on standing in moist air. The rate of this color change depended on the nature of the anion that had been incorporated during the oxidation. The feasibility of faster chemical switching and of color cycling by indirect coulometry was demonstrated. Slow-scan cyclic voltammetry of film specimens on tin oxide electrodes provided
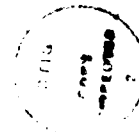
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evidence of incipient phase transitions in blue reduced forms
of the dye. The current-voltage curves could be interpreted on
the basis of a model in which the electron-transfer processes
were assumed to be much faster than the phase transitions. Finally,
the role of oxygen in the dye system was elucidated through discovery
of a reversible oxygen reaction with lutetium diphthalocyanine
in dimethylformamide solution. This information explains some
apparent discrepancies in the chemistry of rare-earth diphthalocyanines
and provides an important link in the formulation of a unified
redox reaction scheme.

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I. INTRODUCTION

This project was part of a continuing investigation into the redox chemistry of the electrochromic rare-earth diphthalocyanines. As thin films on semiconductive tin oxide electrodes, these compounds can assume virtually a full spectrum of colors in response to variation of the electrochemical potential. For that reason, they are of major interest for applications in flat-panel information displays and other electro-optical devices. The experimental work reported here was done with lutetium diphthalocyanine. This dye film is green as initially prepared. Through a series of electron-transfer reactions, it can be converted in discrete steps to orange or red oxidation products and to blue and purple reduction products. Partial conversions lead to intermediate colors. Although much is now known about these reaction processes, they have not yet been fully characterized. In this investigation, several factors governing rates of chemical and electrochemical color conversions in lutetium diphthalocyanine were identified. The chemical processes examined included spontaneous, slow reversion of the oxidized films to the green state in moist air and faster switching of the film colors by contact with aqueous solutions of various oxidizing and reducing agents. The feasibility of color cycling by a technique adapted from indirect coulometry was also demonstrated. In another part of the work, evidence of relatively slow phase transitions in reduced forms of the dye was found by cyclic voltammetry, and a theoretical model was developed to account for the unusual shapes of the current-voltage curves. It was already known from our previous research that ambient oxygen can play a significant role in the diphthalocyanine redox system. The discovery of reversible oxygen addition to lutetium diphthalocyanine under this program provides an important link in the formulation of a unified reaction scheme.

II. STATEMENT OF WORK

a. Lutetium diphthalocyanine dye films will be prepared on transparent conductive and nonconductive substrates by vacuum sublimation.

b. The electrochemistry of the films in aqueous electrolytes will be investigated by coulometric and electro-optical transient methods.

c. The data will be analyzed to determine reaction stoichiometries and rate parameters for electrochromic transformations of the dye.

d. Electrochromic reactions of lutetium diphthalocyanine dye films in contact with liquid electrolyte systems will be investigated by electro-chemical and _in situ_ optical techniques.

e. Direct color conversion rates for electrochemical reactions of the dye will be determined by application of galvanostatic and/or potentiostatic pulses to dye films on electronically conductive substrates.

f. The rates of indirect color conversion by coupled chemical reactions will be investigated with the dye films on open circuit but in close proximity to electrodes at which soluble reactants are electrochemically generated.

III. RESULTS

Results of the experimental research are described below, and some activities for presentation of the conclusions to those concerned with electronic device technology are noted. Items already published elsewhere are given as abstracts only in Parts A, E, and F. Those not previously reported in detail are more fully discussed in Parts B, C, and D.

A. KINETICS OF COLOR REVERSAL IN LUTETIUM DIPHTHALOCYANINE OXIDATION PRODUCTS FORMED WITH DIFFERENT ANIONS[1]

Abstract

The kinetics of color reversal in anodically oxidized lutetium diphthalocyanine films on sapphire was investigated spectrophotometrically. The rate of change from red to green on open circuit in moist air depnded on the anion that was incorporated in the film during the oxidation process. First-order rate constants of approximately 0.1 hr^{-1} were determined for acetate and fluoride films, and 0.003 hr^{-1} was estimated for bromide. Red films containing chloride and sulfate were more stable. Slow oxidation of water by the diphthalocyanine cation is suggested to account for the color reversal.

B. CHEMICAL SWITCHING AND INDIRECT COULOMETRY

The direct electrochemical reactions of lutetium diphthalocyanine films were of primary interest in this project. Under some conditions, however, the observation of those processes is complicated by faradaic reactions of the aqueous electrolyte and by a tendency of the dye to peel away from the substrate. To minimize these problems, indirect coulometry was explored as an alternative means for effecting the color conversions. This technique has been applied by Kuwana et al., to the titration of biological materials in which the redox centers are sterically unable to exchange electrons with an electrode surface.[2] The essential feature of indirect coulometry is the use of soluble electrochemically generated reagents to mediate the electron transfer with the material under investigation. The progress of the reaction is usually followed by in situ absorption spectroscopy.

To demonstrate indirect electrochemical switching of the diphthalocyanine, a transparent generator electrode was placed on the order of tens of microns away from the dye film, parallel to its outer surface. The electrolyte contained, initially, a component of each of two redox couples, one couple having an equilibrium potential more negative than any in the dye system, and the other, an equilibrium potential more positive than any of the dye. On passage of anodic current, an oxidizing agent such as Br_2 was generated. This diffused across the narrow gap and converted the dye to orange or red. The corresponding faradaic charge could be recorded, and the amount of dye converted could be determined from the change in the optical absorption spectrum of the film. The original component, Br^- in this example, was regenerated in the dye reaction. On reverse electrolysis, a component of the other redox couple, such as the methyl viologen dication MV^{2+}, was used to generate a reducing agent MV^+ which returned the dye to the green state, or with continued electrolysis, converted it to a blue form. With no net change in the dye or the coulometric titrants, such color cycles should be repeatable many times.

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Indirect electrochemical cycling through the orange-green-blue range of lutetium diphthalocyanine was demonstrated qualitatively with the Br^-/Br_2 and MV^+/MV^{2+} couples. Since the green form is stable in the presence of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, this couple was usable with Br^-/Br_2 for green/red cycling, or with MV^+/MV^{2+} for green/blue cycling. The green-to-blue reduction process with MV^+ was consistently rather fast in such experiments, but the oxidations using a variety of inorganic reagents tended to be slow and unpredictable, especially with fresh green films prepared by vacuum sublimation.

This problem led us to investigate several pretreatment methods for activating the films. The reactivity was judged by immersing the film specimen directly in the redox medium and visually observing the color change and the time required to produce it. Experimental variables were the type of solid substrate beneath the film, pretreatment by chemical or electrochemical cycling, and the presence or absence of a surfactant.

The results of these chemical experiments are summarized in Table 1. Several trends were noted, and some faster, more predictable reactions were achieved. The dye films on glass tended to peel. A tin oxide substrate was therefore used in most of the tests, even though a conductive support as such was not required, except for cases with electrochemical precycling. The green/orange transition of lutetium diphthalocyanine in chloride media occurs near 0.77 V <u>vs</u> S.H.E. and is independent of pH.[3] Generally, oxidation of the dye was faster with couples having large positive equilibrium potentials. Permanganate, with $E° = 1.49$ V <u>vs</u> S.H.E., destroyed the phthalocyanine ring structure. With the other reagents, the film underwent the usual reversible type of color change. Effects of pretreating the dye film were most pronounced in the range of E° from 0.75 to 1.36 V. Precycling, to orange or red and back to green, was the most effective means of activating the dye film, although the surfactant also promoted the chemical reactions significantly. Quantitative work on indirect coulometry of lutetium diphthalocyanine was initiated

TABLE 1. RESPONSES OF GREEN LUTETIUM DIPHTHALOCYANINE FILMS TO CHEMICAL OXIDIZING AGENTS UNDER VARIOUS CONDITIONS

REAGENT SYSTEM		OBSERVED COLORS AND REACTION TIMES					
		Uncycled Films				Cycled Films[b]	
		Glass Surfactant[a]		Tin Oxide Surfactant[a]		Tin Oxide Surfactant[a]	
Couple	E^0 V vs SHE	Absent	Present	Absent	Present	Absent	Present
Fe^{3+}/Fe^{2+} 0.5M H_2SO_4	0.68	Peeled	Olive 4m	Olive 4m	Olive, slight orange 4m	Olive 4m	Olive 4m
Fe^{3+}/Fe^{2+} 1M $HClO_4$	0.75	Slight olive 4m	Slight olive orange spots 4m	Olive slight orange 4m	Orange 4m	Orange 4m	Orange 4m
Fe^{3+}/Fe^{2+} 1M HCl	0.77	Peeled	Olive 2m	Slight olive 2m	Orange 4m	Orange 2m	Orange 2m
Br_2/Br^- Gaseous	1.09	Olive, 5s Orange, 15s	Orange 15s	Orange 15s	Orange 15s	Orange 15s	Orange 15s
$Cr_2O_7^{2-}/Cr^{3+}$ Acidic	1.35	Orange spots on green 2m	Orange slight olive 2m	Orange-olive 2m	Orange, slight olive 2m	Orange-olive 2m	Orange, slight olive 2m
Cl_2/Cl^- Gaseous	1.36	Olive, 5s orange, 15s	Orange, slight olive 15s	Orange 15s	Orange 15s	Orange 5s	Orange 5s
Ce^{4+}/Ce^{3+}	1.44	Orange, peeling 5s	Orange 5s	Orange 5s	Orange 5s	Orange 5s	Orange 5s
MnO_4^-/Mn^{2+} Acidic	1.49	Gold[c] 10s	Gold[c]; peeling 5s	Gold[c] 5s	Gold[c] 5s	Orange, 3s Gold,[c] 5s	Gold[c] 5s

[a] Surfactant applied as dilute solution of Dow-Corning 193 (silicone glycol ... carbide AL42-12 (imidazoline/tall oil derivative).

[b] Films on tin oxide were electrically cycled; films chemically cycled on glass peeled too severely for further testing.

[c] Gold color was permanent, with destruction of phthalocyanine rings; others faded to green in 1-3 days.

toward the end of the contract period. With pretreatment by a surfactant or by chemical cycling, it should now be possible to investigate chemical reaction rates of dye specimens on insulating substrates such as alumina or transparent plastics which would be selected to maximize adhesion of the organic film.

The comparative difficulty of initiating the chemical oxidations bears further comment. In chemical or electrochemical oxidation, anions must enter the films as charge compensators.[4,5] This apparently requires an expansion of the dye structure to permit the transport of the ions with their associated solvent. For the chemical process, it is not yet known whether a bulky oxidizing species itself must enter the film or whether electron exchange at the solution interface, with transport of the counter ions to the interior, is sufficient. It is noteworthy that the perchlorate counter ion yielded a more stable orange product than the other anions in this series of experiments. With reduction reactions in acidic media, the charge compensators can be hydrogen ions, which are quite small. Hence, if the reducing species such as MV^+ needs only to contact the dye surface, the pretreatment should be less critical for chemical reduction than for chemical oxidation. Our preliminary observations suggest that this is true. Further kinetic studies are needed to characterize the color switching mechanisms in detail.

C. PHASE TRANSITIONS IN REDUCED DIPHTHALOCYANINE FILMS

Galvanostatic transient measurements on the green/red conversion of lutetium diphthalocyanine films in 1 M KCl were reported under a prior AFOSR contract.[6] At current densities of about 1 to 10 mA/cm^2, the results were explained by a two-layer kinetic model with rate control by an ionic space charge in the red oxidized phase.

The dye films were examined by cyclic voltammetry in 0.1 M HCl during the present reporting period. In relatively slow scans, where the peak current densities were on the order of 100 μA/cm^2, factors other than space charge appeared to be rate-controlling. A striking feature was the very sharp pair of current peaks, illustrated by Figure 1, for the dark blue/light blue color conversion. The unusual sharpness of these peaks, combined with their fairly wide separation on the potential scale, suggests that phase transitions accompanied the electrochemical reactions. Similar cases have been discussed, for example, by Bard, et al.[7,8] and by Laviron.[9]

If the phase transitions are slow compared to the electron transfer, such a system can be treated, for slow scanning rates, with two Nernst equations, each modified by the introduction of special activity terms to account for the interactions of species within the solid film. Although a unique model cannot always be developed for a system of this complexity, it is instructive to compare the experimental voltammograms with curves predicted from plausible equilibrium models. Figure 2 includes a comparison of this type for the dark blue/light blue system of lutetium diphthalocyanine. The model was developed along the following lines:

In conventional voltammetry, the potential varies linearly with time. Hence, the current, usually given as $\partial q/\partial t$, can be expressed as $\partial q/\partial E$, which is a more convenient form for use with the Nernst equations. The symbols are q for charge transferred from the beginning of the scan, t for time, and E for
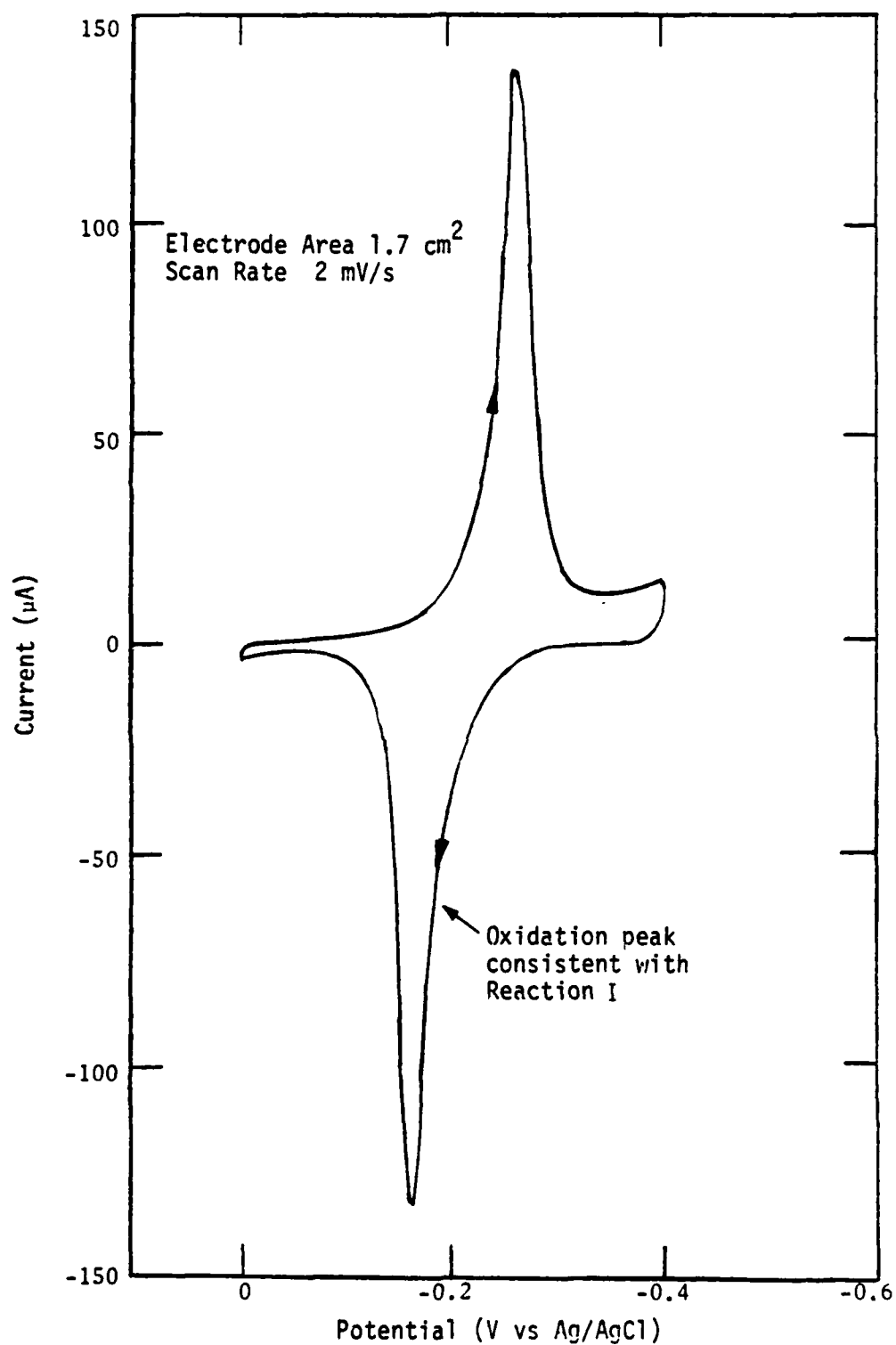
Figure 1. Linear-Potential-Sweep Voltammogram for Light Blue/
Dark Blue Transition of Lutetium Diphthalocyanine
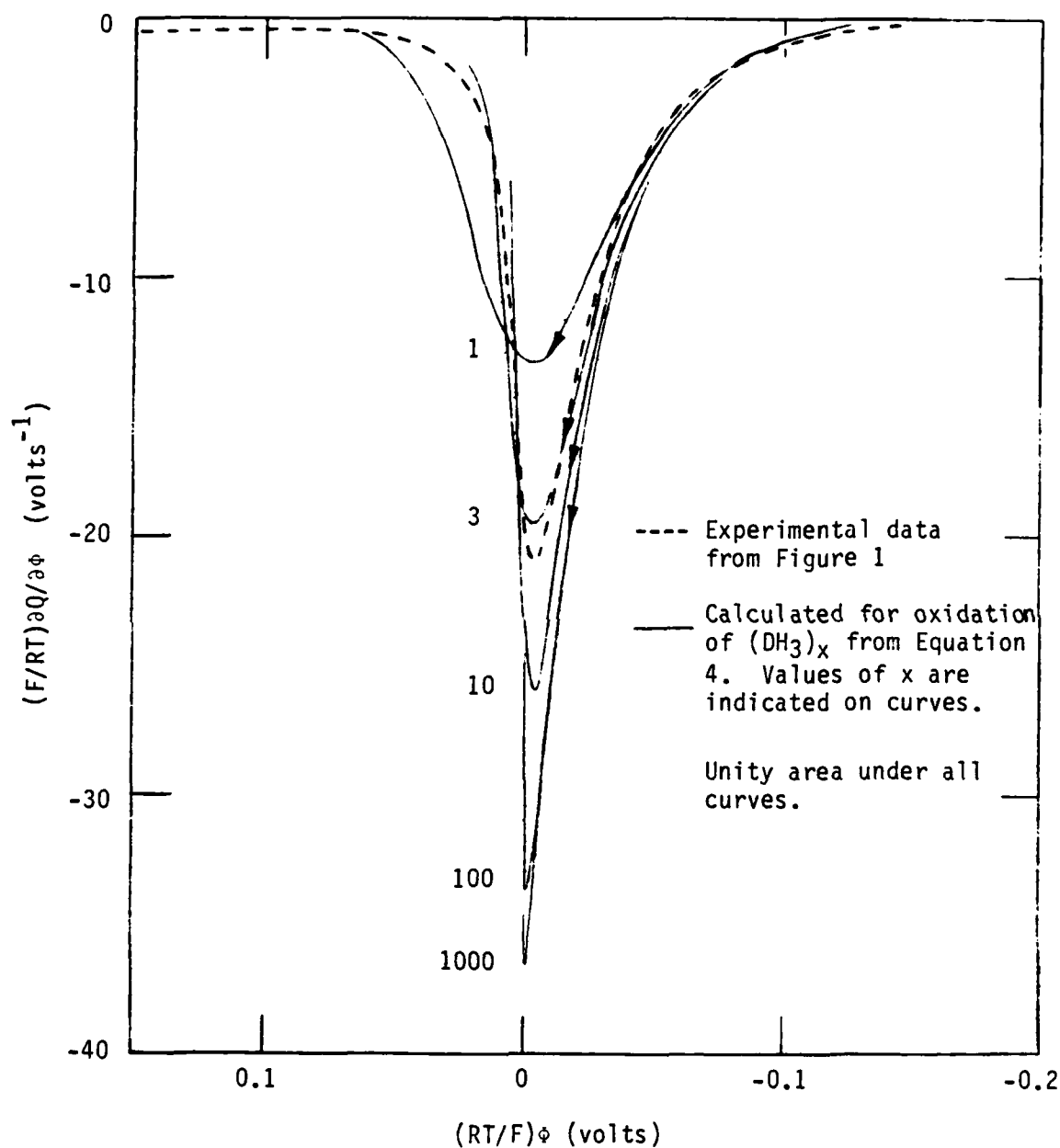in 0.1 M HCl

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Figure 2. Experimental and Theoretical Voltammograms for Oxidation of Dark Blue to Light Blue Form of Lutetium Diphthalocyanine.

the potential of the working electrode on a selected reference scale. This formulation is conceptually akin to that in the recently developed technique of derivative linear-sweep voltabsorptometry, in which the cumulative faradaic charge is found from the optical absorbance of the oxidized or reduced species.[10] As a further convenience in comparing the shapes of the volt-ammograms, the plots were normalized to unit area beneath the curves. This was done by defining a dimensionless charge Q as

$$Q = q/q_{lim} \tag{1}$$

where q_{lim} is the limiting charge required for complete conversion of the film. Then

$$\int_{-\infty}^{\infty} (\partial Q/\partial E)dE = 1 \tag{2}$$

Several models for partially associated dark blue products were investigated by computer simulation. The model represented in Figure 2 was based on the reaction

$$(DH_3)_x(s) \rightleftharpoons xD^-(s) + xH^+(s) + 2xH^+(1) + 2xe \qquad I$$
$$\text{Dark Blue} \qquad \text{Light Blue}$$
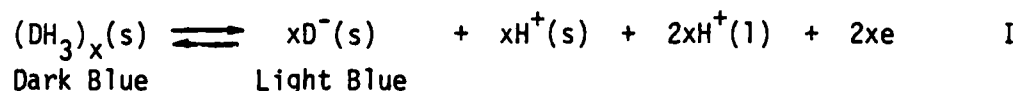
where (s) and (1) denote species in the solid and liquid phases and the symbol D represents a green form of the dye, now thought to be $LuPc_2$ (Section III-D). With constant pH in the electrolyte, the variable activities were taken to be the volume concentrations of $(DH_3)_x(s)$, $D^-(s)$, and $H^+(s)$ in the solid film.

The equations were set up so that quantity Q designated the cumulative anodic charge passed from the beginning of the positive scan. Then, for a

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degree of association x in Reaction I, a dimensionless potential Φ was identified as

$$\Phi = \ell n(1-Q) - (1/2x)\ell nQ \qquad (3)$$

By differentiation of Equation (3), the voltammetric curve at an infinitesmal scanning rate was found to have the form
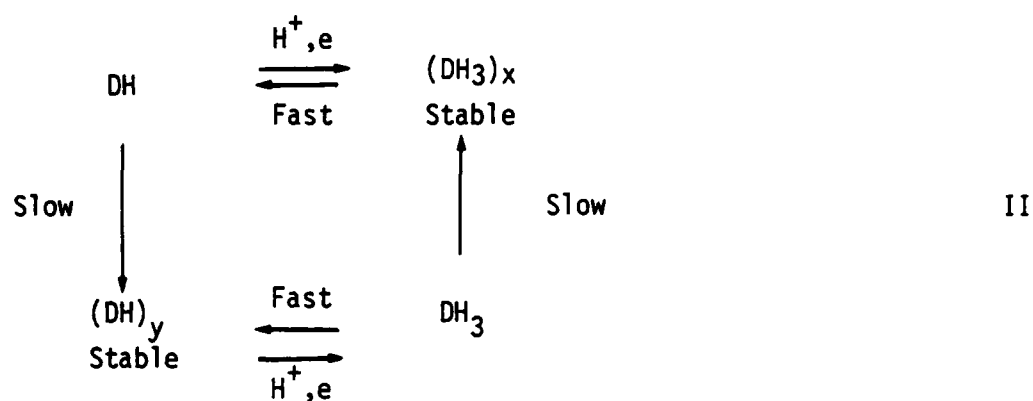
$$\partial Q/\partial \Phi = 2xQ(1-Q)/[2xQ + (1-Q)] \qquad (4)$$

The potential scale is expressible in volts through the relationship

$$dE = (RT/F)d\Phi \qquad (5)$$

The experimental oxidation curve in Figure 1 was arbitrarily positioned to make the peak potential coincide with that of the calculated curve. Reaction I implies that the light blue form DH, or $LuHPc_2$, is ionized in the solid phase, while the dark blue DH_3 is not. It has since been found in a related investigation that these reduced forms at pH < 4 apparently are acid adducts with the respective compositions $DH \cdot 2HCl$ and $DH_3 \cdot 6HCl$.[3] Hence, Reaction I may be oversimplified, although the agreement of the data with the calculated curve for x = 3 is rather close.

The cathodic curve would be a mirror image of the anodic if Reaction I applied to the reduction process as well. Instead, the two experimental curves of Figure 1 are reversed in shape from right to left, and the peaks are separated by 0.10 V. We interpret these differences as evidence of association in the light blue phase from the outset of the cathodic scan, just as DH_3 appeared to be associated from the beginning of the anodic scan. In other words, the system may participate in a "square" reaction scheme of a type proposed by Peerce and Bard for films containing nonequivalent redox sites.[7] Then the dye reactions could be represented by the scheme

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$$DH \underset{\text{Fast}}{\overset{H^+,e}{\rightleftharpoons}} (DH_3)_x \quad \text{Stable}$$

Slow $\downarrow$ (DH)$_y$ Stable $\qquad$ Slow $\uparrow$ DH$_3$ $\qquad$ II

$$(DH)_y \underset{H^+,e}{\overset{\text{Fast}}{\rightleftharpoons}} DH_3$$

Further research is needed to characterize the voltammetric behavior more specifically and relate it to the pH dependence. However, the qualitative interpretation based on incipient phase transitions probably is valid.

D. ROLE OF OXYGEN IN THE DYE REACTION SCHEME

Most metal phthalocyanines may be considered salts of the metal-free dye compound H_2Pc. Accordingly, the green diphthalocyanines of the lanthanide elements (Ln) originally were assumed to have the formula $LnHPc_2$, in which the metal is trivalent and one labile hydrogen remains.

However, two kinds of experimental evidence from other laboratories indicate the radical form $LuPc_2^{\cdot}$, rather than $LuHPc_2$, for the green lutetium complex. First, green solutions in organic solvents and green solid preparations are paramagnetic.[11-13] Second, the mass spectrum corresponds to $LuPc_2$,[12,14] although some $LuHPc_2$ has also been detected recently by mass spectrometry with the field desorption technique.[14]

The assumption of different formulas for the initial green material has necessarily led to the proposal of many different products in the redox reaction scheme.[15] The problem is further complicated by the finding of nonintegral faradaic n values in some of the electrochemical experiments[4,6] and by the observation of interconvertibility between the blue and green forms of the diphthalocyanines during chromatographic separations.[16] In a review article, we suggested that the forms $LuPc_2$ and $LuHPc_2$ may be convertible through the reaction

$$LuPc_2 + 1/2\ H_2O \rightleftharpoons LuHPc_2 + 1/4\ O_2 \qquad\qquad III$$
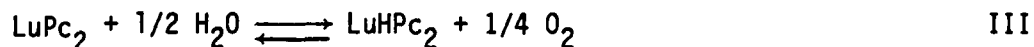
and proposed oxygen complexes such as $LuHPc_2 \cdot O_2$ or $LuHPc_2^+\ O_2^-$ to account for the paramagnetism of green preparations exposed to air.[15] Our prior research had also demonstrated sensitivity to oxygen in certain cases where green/red reaction boundaries were propagated anodically in insulator-supported films contacted by aqueous electrolytes.[17]

In this AFOSR project we obtained direct evidence, by optical absorption spectroscopy, of oxygen complexation with the dye. This interaction was

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observed with freshly sublimed green films of lutetium diphthalocyanine.
Moreover, a reversible reaction with oxygen was demonstrated for solutions of the
dye in dimethylformamide. This new information provides an important link in
the redox reaction scheme and explains a number of puzzling observations.
The experimental results and interpretations are given below.

The behavior of the vacuum-sublimed films toward oxygen depended on the
thermal history of the specimens. Curve (a) in Figure 3 is the spectrum of a
fresh film deposited on an <u>unheated</u> glass substrate, recorded under nitrogen
without prior exposure to air. We now believe this to be the spectrum of
$LuPc_2$. On admission of air, the spectrum changed to Curve (b), which is
characterized by a sharp increase and a slight wavelength shift in the main
peak near 670 nm, and by the appearance of vibrational bands at 575 and 600 nm.
The smaller peak near 460 nm was also shifted slightly. When the film was
deposited on a substrate <u>preheated</u> with an infrared lamp, the initial spectrum
essentially matched Curve (a) but no change occurred on exposure to air. The
spectrum (b) of the air-exposed specimen also reverted to the form of (a) on
heating, and the air sensitivity was lost. These results suggest that two
forms of $LuPc_2$ can exist: A heated form, which may be more crystalline or
loosely polymerized and shows no spectral change on exposure to air, and an
unheated form which can react with oxygen and/or water in the air. In fact,
Collins and Schiffrin have found roughly stoichiometric amounts of oxygen in
unheated lutetium diphthalocyanine films by X-ray photoelectron spectroscopy,[14]
while in this project, we observe substantial quantities of water in such films
by mass spectroscopy.

Absorption spectra were also recorded under several conditions for lute-
tium diphthalocyanine dissolved in dimethylformamide (DMF), dimethyl sulfoxide
(DMSO), dichloromethane, or acetone. The DMF system, represented by Figure 4,
proved to be of greatest interest, since it provided strong evidence of rever-
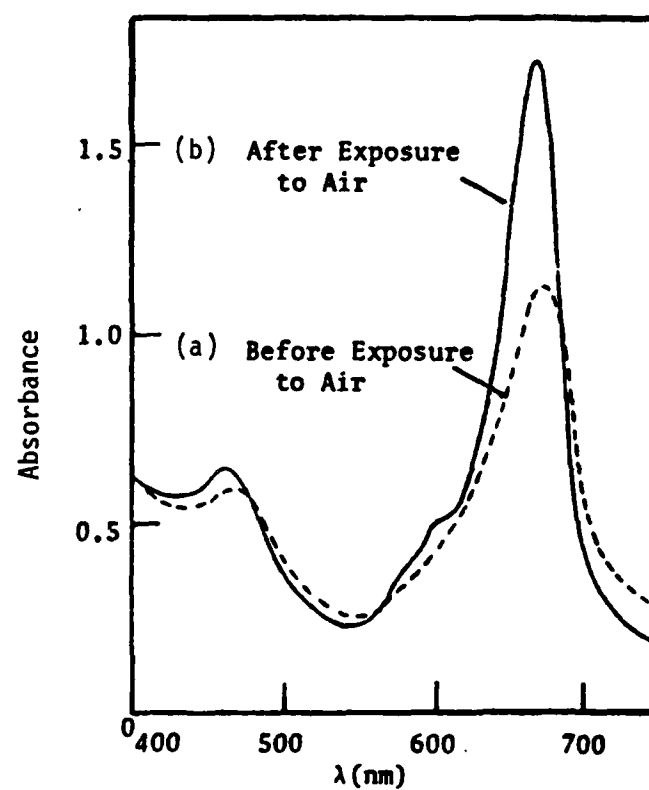sible oxygen addition at room temperature.

Figure 3. Effect of Air on Spectrum of Lutetium Diphthalocyanine
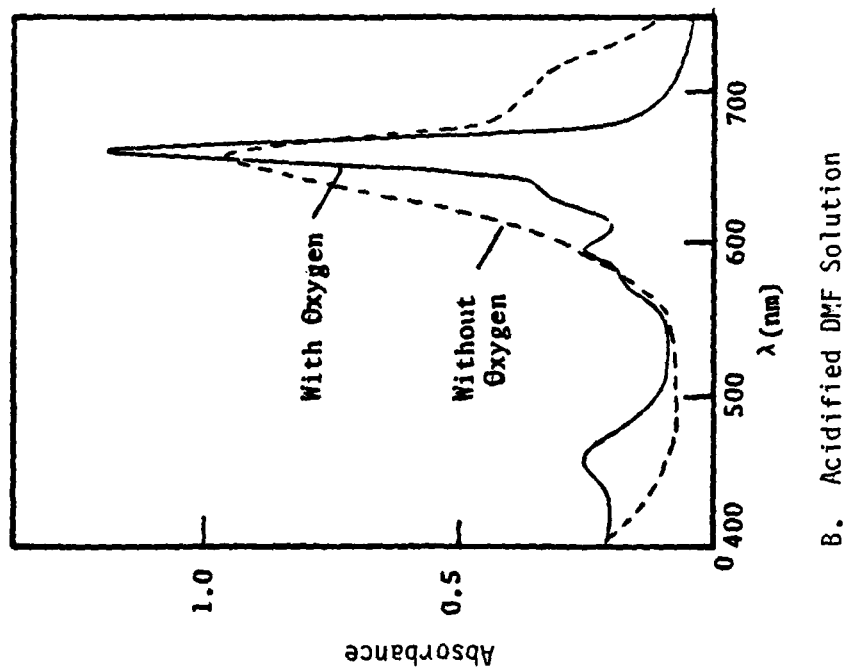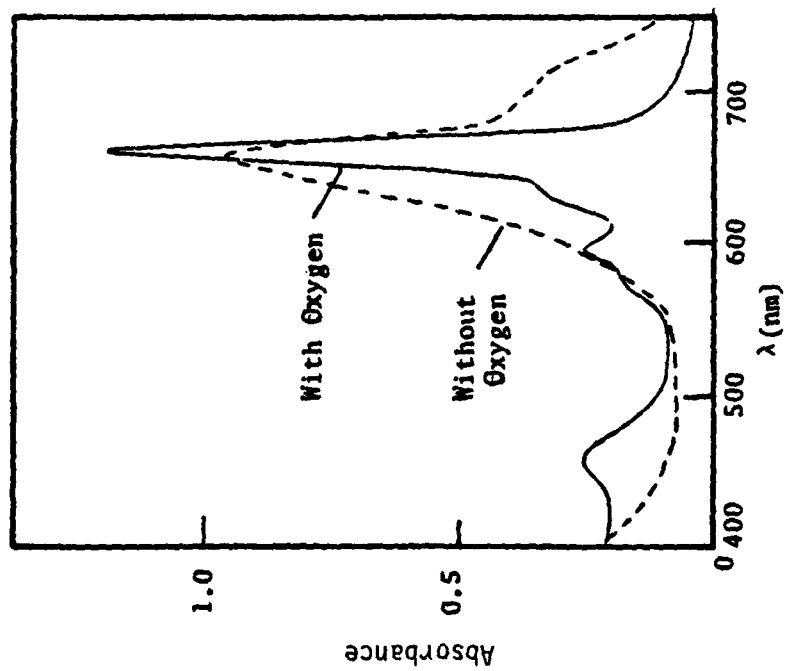Film Vacuum-Sublimed on Unheated Glass Substrate

Figure 4. Effects of Oxygen on Spectra of Lutetium Diphthalocyanine Solutions in Dimethylformamide
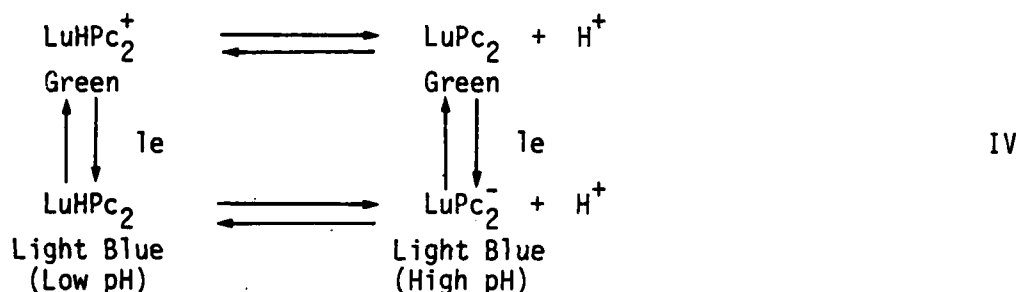
Figure 4A shows the usual double-peak spectrum obtained by dissolving the green dye in reagent grade DMF that has not been specially purified. Corker et al. were the first to point out that this blue solution could be a reduction product of the green form resulting from its reaction with aliphatic amine impurities.[11] They also showed that the paramagnetic green form was retained on dissolution in DMF that had been distilled over $CuSO_4$ or pre-electrolyzed. In the present work, we obtained the same green spectrum, shown as the solid line in Figure 4B, by adding a small amount of aqueous HCl to the blue solution of Figure 4A. This curve, recorded in the presence of oxygen, is the typical spectrum of the paramagnetic green reported by Corker et al. and by Chang and Marchon.[12] It also closely resembles the spectrum of the un-heated air-exposed film in Figure 3.

After the acidified DMF solution was purged with helium , the spectrum changed to the broken line of Figure 4B, which is that of a blue form, distinct from the nonacidified blue of Figure 4A. Significantly, the change from blue to green in acidified DMF was reversible with addition and removal of oxygen. A similar effect was observed in unpurified DMSO, but the addition of oxygen was not reversible. Related changes due to oxygen also occurred in acidified acetone, with possible appearance of an intermediate not yet characterized. The spectrum in CH_2Cl_2 (without acid) was consistently that of the oxygenated green form.

The three solution spectra of lutetium diphthalocyanine in DMF, and the dry-film spectrum with oxygen, are identifiable with certain film spectra that we obtained in an electrochemical study of pH-potential relationships under a related Navy contract.[3] With these correlations and magnetic data from other laboratories, a more complete redox scheme can now be written. A central point is the spectral similarity between the oxygen-containing green film, the oxygenated green in acidified DMF, and the electrochemically cycled green in the absence of oxygen. For all of these green forms, we propose

the paramagnetic cation form $LuHPc_2^+$, which is a protonated version of $LuPc_2$. This cation can occur in combination with the superoxide ion O_2^- or with another anion such as Cl^-; hence the identity of the oxygenated and cycled green dye species.

The spectrum of the blue form with or without oxygen in nonacidified DMF approaches that of the light blue 1-electron reduced dye film at pH 7.2, while that of the acidified blue in oxygen-free DMF resembles the 1-electron reduced-film spectrum at pH 1.[3] The acid-base and green/light blue redox equilibria appear to be related through the scheme

$$
\begin{array}{ccc}
LuHPc_2^+ & \rightleftharpoons & LuPc_2 \; + \; H^+ \\
\text{Green} & & \text{Green} \\
\updownarrow \; 1e & & \updownarrow \; 1e \\
LuHPc_2 & \rightleftharpoons & LuPc_2^- \; + \; H^+ \\
\text{Light Blue} & & \text{Light Blue} \\
\text{(Low pH)} & & \text{(High pH)}
\end{array}
\qquad \text{IV}
$$

Finally, a discrepancy in the anodic n values of earlier experiments can be resolved. Nonintegral n's approaching 2 typically resulted from anodic boundary propagations in air,[4] while values close to 1.0 were found by an incremental potential-step technique, using cycled films in the absence of air.[3] This difference can be explained on the basis of $LuHPc_2^+ \, O_2^-$ as the predominant starting material in the boundary propagations. This structure is analogous to $MnPc^+ \, O_2^-$ proposed by Lever, Wilshire, and Quan for the dioxygen adduct formed with MnPc in dimethylacetamide.[18] The superoxide ion O_2^- is a relatively strong reducing agent.[19] Hence the over-all anodic reaction for an air-exposed lutetium diphthalocyanine film should be

$$
LuHPc_2^+ \, O_2^- \; + \; 2X^- \longrightarrow LuHPc_2^{2+} \cdot 2X^- \; + \; O_2 \; +2e \qquad \text{V}
$$

$$
\text{Green} \qquad\qquad\qquad \text{Orange}
$$
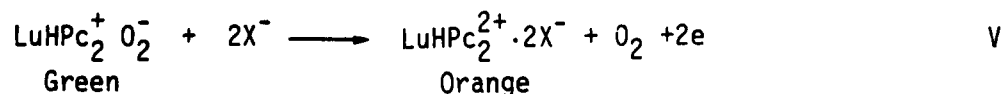
in an electrolyte with the anion X^-. For a <u>cycled</u> green film in the absence of air, however, the same color conversion would require only one electron:

$$LuHPc_2^+\,X^- \;+\; X^- \longrightarrow LuHPc_2^{2+} \cdot 2X^- + e \qquad\qquad VI$$

Green   Orange
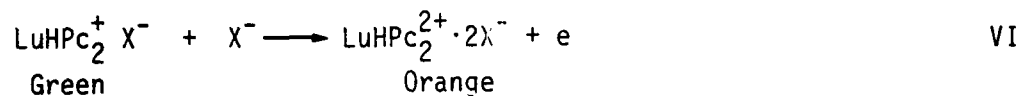
A journal manuscript reporting the reversible oxygen addition to $LuHPc_2$ and its implications for the diphthalocyanine redox system is in preparation.

E.   ELECTROCHROMICS[20]

The principal investigator was invited to write the article on electro-
chromics for the Encyclopedia of Materials Science and Engineering, to be
published by Pergamon Press in 1983. In condensed style, this paper describes
electrochromic display devices and their operating mechanisms and compares
the electrochromic materials tungsten oxide, iridium oxide, n-heptyl viologen
bromide, rare-earth diphthalocyanines, and synthetic polymers. Highlights of
research and development in this field are also noted.

F. MULTICOLOR ELECTROCHROMIC DISPLAY TECHNOLOGY[21]*

Abstract

Multicolor flat-panel displays that are easily read in bright ambient light are essential to most advanced cockpit designs. The electrochromic technology described uses a film of rare-earth diphthalocyanine dye material which changes to various colors in response to small applied dc voltages. Fundamentally, the writing and erasure processes resemble the charging and discharging of a battery, and, like a battery, the device retains its state of charge, or memory, on open circuit. The image can be viewed with front or back lighting or projected on screen. The cell structure, performance, electrochemical switching mechanism, and drive requirements are discussed, and some results of a recent color-enhancement study are presented.

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VI. PRESENTATION

M. M. Nicholson and T. P. Weismuller, "Multicolor Electrochromic Display Technology," IEEE National Aerospace and Electronics Conference, Dayton, Ohio, May 1983.

VII. PROJECT PERSONNEL

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